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LETTER TO THE EDITOR

Reaction of the Oxygen Radical Anion O^- with Water on the FeZSM-5 Zeolite Surface

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The oxygen radical anion O^- has attracted considerable attention as a reactive species capable of participating in catalytic oxidation reactions [1–7]. In view of this, zeolite FeZSM-5, which shows excellent catalytic properties in a number of oxidation reactions involving N_2O, is of special interest. A special feature of this catalyst is the presence of specific sites that are mononuclear Fe^{2+} complexes (alpha sites) stabilized in the zeolite matrix. The alpha sites are not oxidizable by molecular oxygen, but are readily oxidizable by nitrous oxide, yielding the radical anion O^-, which is called α-oxygen in this system [5–7]:

$$(Fe^{2+})_\alpha + N_2O \longrightarrow (Fe^{3+}\text{–}O^-)_\alpha + N_2. \quad \text{(I)}$$

Like O^- on vanadium and molybdenum oxides [1–4], α-oxygen is highly reactive, showing a marked ability to abstract hydrogen from the molecules being oxidized. In addition to being practically important, zeolite FeZSM-5 is a convenient model for the study of the O^- radical anion, whose concentration in this system can exceed, by 2–3 orders of magnitude, their concentration on the surface of an ordinary oxide catalyst.

In this letter, we report an earlier unknown reaction that we discovered when investigating water adsorption on zeolite FeZSM-5 containing α-oxygen:

$$2(Fe^{3+}\text{–}O^-)_\alpha + H_2O \longrightarrow 2(Fe^{3+}\text{–}OH^-)_\alpha + 1/2O_2. \quad \text{(II)}$$

As in the case of methane, ethane, and other hydrocarbons, the reaction between $(O^-)_\alpha$ and water occurs via a hydrogen abstraction mechanism, yielding hydroxyl groups on alpha sites and releasing the equivalent amount of oxygen into the gas phase.

The reaction between $(O^-)_\alpha$ and water was carried out in a static vacuum apparatus fitted with a mass spectrometric gas analyzer. After completion of the experiment, water was frozen out into a liquid nitrogen trap and the amount of O_2 released was measured. It can be seen from the table that the amount of oxygen does not depend on temperature and in all cases equals 0.40–0.45 of the initial amount of α-oxygen. This value is close to the stoichiometric coefficient 0.5 in reaction (II). The underestimation of the amount of dioxygen in these experiments is likely caused by small oxygen losses, which may be due to partial oxygen capture into frozen water.

Table

Entry	Initial amount of $(O^-)_\alpha$, 10^{18} atom/g	H_2O adsorption temperature, °C	H_2O pressure, Torr	Amount of O_2 released, 10^{18} atom/g
1	17	25	4	8.0
2	17	50	4	7.0
3	18	100	2	8.0
4	17	125	2	7.0
6	18	200	2	7.0

Reaction (II) is confirmed by IR spectroscopy, TPD, and experiments involving the isotope ^{18}O.

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